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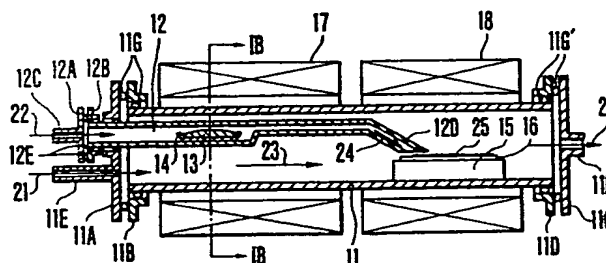
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⑤④ Epitaxial growth method and apparatus therefor.

⑤⑦ In an epitaxial growth method, a first gas (21) consisting of a hydrogen diluted gas containing a Group V element is continuously flowed on a monocrystalline substrate (16) that is placed in a reaction chamber, the monocrystalline substrate (16) is arranged in a gas mixing region where the first gas and a second gas containing a halogenide of a Group III element are mixed adjacent to the monocrystalline substrate, and a Group III-V compound semiconductor (25) is grown on the monocrystalline substrate.



Specification

Title of the Invention

Epitaxial Growth Method and Apparatus Therefor

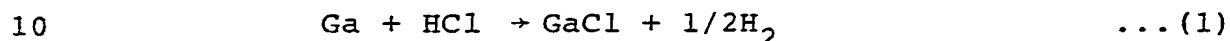
5 Background of the Invention

The present invention relates to a method and apparatus for epitaxially growing a Group III-V compound semiconductor on a monocrystalline substrate.

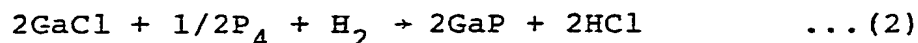
As method^S for epitaxially growing a Group III-V
10 compound semiconductor on a monocrystalline substrate, a vapor phase epitaxy (VPE) method, a metal organic chemical vapor deposition (MOCVD) method, and a molecular beam epitaxy (MBE) method are known. In a hydride VPE method, a Group III material is converted^{to} to a halogenide, and is
15 supplied into a reaction tube together with H₂ diluted gas containing a Group V element so as to grow a Group III-V compound semiconductor on a substrate. By this method, in the case of homo-epitaxial growth wherein a crystal is grown on a substrate of the same type material, a
20 crystalline film having a high purity and good crystallinity can be easily obtained. Therefore, this method is widely applied to the manufacture of a Group III-V compound (e.g., GaAs, GaP, InP, and the like) semiconductor device.

25 The conventional hydride VPE method in the case of GaP growth will now be described with reference to Figs. 11(A) and 11(B). Ga 3 of a Group III material stored

in a boat 2 and a GaP monocrystalline substrate 4 are arranged inside a reaction tube 1. An electrical oven (not shown) is arranged around the reaction tube 1, so as to keep the temperature distribution inside the reaction tube, as shown in Fig. 11(B). A gas mixture 6 containing PH_3 and H_2 is introduced from an introduction tube 5 inside the reaction tube and a gas mixture 7 containing HCl and H_2 is introduced through a gas inlet (not shown). The introduced HCl reacts with the heated Ga as follows.

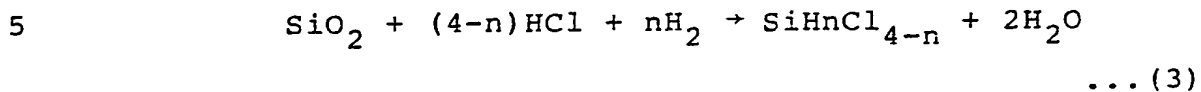


A gas mixture 8 containing H_2 and GaCl produced by the reaction given by reaction formula (1) is supplied toward the downstream side. PH_3 is decomposed into P_4 and is mixed with the gas mixture 8 containing GaCl and H_2 in a baffle 9 placed on a high-temperature area, thereby forming a gas mixture 10 containing P_4 , GaCl , and H_2 . The gas mixture 10 passes the high-temperature region and then flows into the low-temperature region. As the temperature of gas mixture 10 is reduced, GaP grows on the GaP monocrystalline substrate 4 placed on the low-temperature region by the reaction expressed by reaction formula (2).



In the case of homo-epitaxial growth wherein GaP is to be grown on the substrate 4 of a GaP single crystal, GaP can be grown epitaxially as described above. When an Si single crystal is used as the substrate 4, GaP cannot be grown for the following reasons. The reaction tube is

normally made of silica glass (SiO_2) because of its good heat ^{process} ~~ability~~, and working ^{properties} ~~properties~~. When HCl is brought into contact with the silica glass which is heated to high temperature, H_2O is produced by the following reaction:



(where $n = 0$ to 3)

H_2O is supplied above the Si substrate on the downstream side together with the H_2 gas and reacts with Si, thereby producing SiO_2 . The thus produced SiO_2 covers the Si substrate surface and prevents the GaP growth on the Si substrate.

The article of H. Huber and G.H. Winstel (Siemens Forschungs und Entwicklungsberichte; 2 (1973) pp. 171-174) describes an example wherein an electrical oven for annealing is provided in addition to the electrical growth oven, the Si substrate is annealed in the H_2 atmosphere to remove a natural oxide film, and immediately thereafter, the substrate is moved to a growth region so as to grow GaP. However, in this case, since the substrate is exposed to the HCl atmosphere at ^ahigh temperature of about 800°C , a formation of SiO_2 on the Si substrate cannot be avoided. For this reason, ^{the}growth reproducibility is poor, and even if grown, the resultant crystal has a poor crystallinity and cannot be used as a substrate of practical device.

For the above reasons, the hetero-epitaxial growth of the Group III-V compound semiconductor on the Si

substrate has not yet been realized by the epitaxial growth method containing halogenide such as HCl.

There are several attempts to grow^a Group III-V compound semiconductor on^a Si substrate by the MOCVD or MBE.

5 However, these methods cannot provide a crystal having crystallinity comparable to that of a crystal which is homo-epitaxially grown by the epitaxial growth method containing a halogenide.

M. Akiyama et al. reported a GaAs crystal which
10 is grown on an Si substrate by the MOCVD method (Journal of Crystal Growth, Vol. 68, pp. 21-26, 1984). With this report, a GaAs film which was deposited on the Si substrate by decomposing trimethyl gallium and AsH₃ at 400°C was annealed at 750°C, and mirror-surface-like monocrystalline
15 GaAs could be obtained. However, even when GaAs was grown on the resultant GaAs film by a conventional method, such as the MOCVD or hydride VPE method, the resultant crystal could not provide the same crystallinity as that of a crystal which was grown on a GaAs substrate. It was
20 revealed by an impurity analysis in the depth direction of the resultant film that CH₃ as a constituting molecule of trimethyl gallium is left in the film without being decomposed and degrades the crystallinity since a first film is deposited at a low temperature of 400°C.

25 Attempts for developing a device for integrating many or various functions on an identical substrate have been made. For example, an optical-electronic device in

which optical devices and electronic devices are integrated on an identical substrate is known. When devices made of different materials are integrated on an identical substrate, in order to fabricate the next device so as not to impair the previously fabricated device, the steps for growing the respective materials must be performed at low temperature. However, in the conventional method, when growth is carried out under the condition of decreased substrate temperature, a crystal is deposited on a region of the inner wall of the reaction tube corresponding to a temperature, at which the growth is conventionally performed, on the upstream side of the substrate position, and no crystal is grown on the substrate. In this manner, hetero-epitaxial growth for integrating many or various functions on an identical substrate cannot be grown by the conventional hydride VPE method.

Summary of the Invention

It is a principal object of the present invention to provide an epitaxial growth method and an apparatus therefor, ^{by} which the growth ^{ing of} of a Group III-V compound semiconductor of high quality on a monocrystalline substrate can be achieved.

It is another object of the present invention to provide an epitaxial growth method and an apparatus therefor, ^{by} which the growth ^{ing of} of a uniform Group III-V compound semiconductor on a monocrystalline substrate can be achieved.

In order to achieve the above objects, there is provided an epitaxial growth method wherein a first gas consisting of a hydrogen diluted gas containing a Group V element is continuously flowed on a monocrystalline substrate that is placed in a reaction chamber, the monocrystalline substrate is arranged in a gas mixing region where the first gas and a second gas containing a halogenide of a Group III element are mixed adjacent to the monocrystalline substrate, and a Group III-V compound semiconductor is grown on the monocrystalline substrate.

According to another aspect of the present invention, there is provided an epitaxial growth method comprising: the first step of flowing a first gas consisting of a hydrogen diluted gas containing a Group V element on a monocrystalline substrate that is placed in a reaction chamber, flowing a second gas containing a halogenide of a Group III element along a flow path different from that of the first gas, placing the monocrystalline substrate on a gas mixing region where the first and second gases are mixed, and growing a Group III-V compound semiconductor on the monocrystalline substrate; and the second step of further growing a Group III-V compound semiconductor on the Group III-V compound semiconductor grown by the first step.

According to still another aspect of the present invention, there is provided an epitaxial growth apparatus comprising: a first flow path, formed in a reaction

chamber, for flowing a first gas consisting of a hydrogen diluted gas containing a Group V element; a second flow path, formed in the reaction chamber, for flowing a second gas containing halogenide of a Group III element; and a support member for a monocrystalline substrate arranged in the reaction chamber, end portions of the first and second flow paths in the reaction chamber being arranged so as to constitute a mixing region where the first and second gases are mixed, and the support member displacing the monocrystalline substrate in the mixing region, so as to allow growth of a Group III-V compound semiconductor on the surface of the monocrystalline substrate.

Brief Description of the Drawings

Figs. 1(A) and 1(B) show an epitaxial growth apparatus according to an embodiment of the present invention, in which Fig. 1(A) is a sectional view taken along a longitudinal direction of the apparatus, and Fig. 1(B) is a sectional view taken along a line IB-IB in Fig. 1(A);

Fig. 1(C) is a graph showing a temperature distribution of the apparatus;

Figs. 2(A) to 2(D) are reflection high energy electron diffraction (RHEED) photographs of a GaP crystal which is grown by the method of the present invention;

Fig. 3 is a graph showing the relationship between a growth time and a film thickness of GaP which is grown on an Si (111) substrate;

Figs. 4(A) and 4(B) show an epitaxial growth apparatus according to another embodiment of the present invention, in which Fig. 4(A) is a sectional view taken along a longitudinal direction of the apparatus, and
5 Fig. 4(B) is a sectional view taken along a line IVB-IVB in Fig. 4(A);

Fig. 5 is a graph showing semiconductor growth rate characteristics in a gas mixing region and a downstream side region thereof;

10 Fig. 6 is a graph showing the relationship between a film thickness of GaP grown on an Si (100) substrate and a PH_3 flow rate;

Fig. 7 is a graph showing the relationship between a film thickness of GaP grown on an Si (100) substrate and a substrate temperature;
15

Figs. 8(A) to 8(C) are reflection electron beam diffraction photographs of a GaP crystal which is grown on an Si (100) substrate by two-step growth of the present invention;

20 Fig. 9 is a graph showing the relationship between a substrate covering ratio with a GaP layer and a substrate temperature;

Figs. 10(A) and 10(B) are sectional views showing an epitaxial growth apparatus according to still another embodiment of the present invention;
25

Fig. 11(A) is a sectional view of a conventional epitaxial growth apparatus; and

Fig. 11(B) is a graph showing a temperature distribution of the apparatus shown in Fig. 11(A).

Description of the Preferred Embodiments

Example 1

5 An embodiment of the present invention will now be described with reference to the accompanying drawings.

Figs. 1(A) and 1(B) show an epitaxial growth apparatus according to an embodiment of the present invention, and Fig. 1(C) shows a temperature distribution
10 in the apparatus. Referring to these figures, a reaction tube 11 which is made of silica glass constitutes a double tube structure together with a Group III element source chamber (to be referred to simply as a source chamber hereinafter) 12 made of silica glass. The reaction tube 11
15 need not have a cylindrical shape as shown in Fig. 1(B) but may ^{well} have ^{any} other sectional shapes. The sectional shape of the source chamber 12 need not be ^{of} a semicircular shape as shown in Fig. 1(B) but can be ^{of any} other suitable shape such as a rectangular shape. The two ends of the reaction tube 11
20 are shielded from an outer atmosphere, respectively, by a lid 11A, a flange 11B, and an O-ring 11G, and a lid 11C, a flange 11D, and an O-ring 11G'. A gas inlet 11E is formed on the lid 11A, and a gas outlet 11F is formed on the lid 11C. One end portion of the source chamber 12 is shielded
25 from an outer atmosphere by a lid 12A, a flange 12B, and an O-ring 12E. A gas inlet 12C is formed on the lid 12A. The other end portion of the source chamber 12 has an opening

portion 12D which is open to the reaction tube 11. The opening portion 12D has a downwardly inclined portion, and its opening end is formed to be substantially parallel to the surface of a substrate (to be described later) which is arranged therebelow. A Group III element 13 is stored in the source chamber 12 while being housed in a boat 14. A substrate support table 15 is arranged below the opening portion 12D in the reaction tube 11, and a substrate 16 on which a crystal is to be grown is supported thereby.

10 Reference numerals 17 and 18 denote electrical ovens for heating the reaction tube 11. The seal method of the two ends of the reaction tube 11 and locations of the gas inlet and the gas outlet are not limited to those illustrated in Figs. 1(A) and 1(B), and various other known methods can be used.

15

A method for growing GaP on an Si monocrystalline substrate having a (111) plane using the apparatus shown in Figs. 1(A) and 1(B) will now be described.

Ga is used as the Group III element 13. The surface of the Si substrate 16 having a (111) plane is cleaned by chemical etching or the like, and a natural oxide film formed on the surface is removed by a hydrogen fluoride (HF) solution. Then, the substrate 16 is set on the substrate support table 15. A gas mixture 21 containing phosphine (PH_3) and hydrogen (H_2) as source materials of a Group V element is introduced from the gas inlet 11E into the reaction tube 11, and an H_2 gas 22 is

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introduced from the gas inlet 12C into the source chamber 12. After ^{the} air inside the apparatus has been sufficiently substituted by the introduced gases, the reaction tube 11 is heated. The temperature distribution of the reaction tube 11 is as shown in Fig. 1(C). More specifically, the electrical ovens 17 and 18 are controlled such that high temperature is obtained at the position of the Ga 13 and low temperature is obtained at the position of the substrate 16. When ^{the} desired temperature distribution is obtained, e.g., when a Ga temperature (T_G) reaches 500°C to 900°C, preferably, 750°C to 850°C and a substrate temperature (T_G) reaches 400 to 800°C, preferably, 600°C, hydrogen chloride (HCl) gas is ^{supplied} from the gas inlet 12C to convert the gas flow 22 to be a gas mixture containing (HCl + H₂). PH₃ contained in the gas flow 21 is decomposed by heat to be ^{come} a gas flow 23 containing (P₄ + H₂). Meanwhile, HCl produces GaCl by reaction given by reaction formula (1) and forms a gas flow 24 containing (GaCl + H₂). The gas flow 24 containing the Group III element Ga and the gas flow 23 containing the Group V element P flow along independent flow paths, and are mixed near the opening portion 12D of the source chamber 12. Thus, a GaP crystal 25 is grown on the substrate by a reaction given by reaction formula (2). An exhaust gas 26 is exhausted from the gas outlet 11F.

With the method of this example, the substrate surface before crystal growth is exposed to a (PH₃ + H₂) or

($P_4 + H_2$) atmosphere and, hence, will not be oxidized. GaCl and P_4 pass a high temperature region separately, and produce GaP near the low-temperature substrate. Therefore, a high degree of super saturation of crystal growth can be realized, and hence, a high growth rate can be achieved. The atmosphere surrounding the substrate has a low oxygen content, and H_2O produced by ^areaction given by reaction formula (3) reaches the substrate after the growth of the crystal. Therefore, the substrate will not be oxidized, and the GaP crystal <onto the Si substrate> can grow satisfactorily. < >

The Si substrate 16 is located immediately below the opening portion 12D. A distance between the substrate surface and the opening portion 12D is preferably as short as possible so as not to interfere with the reaction given by reaction formula (2) after the gas flows 23 and 24 are mixed. In this example, the distance from the surface of the substrate 16 to the opening portion 12D is about 2 mm.

The GaP crystal growth starts upon introduction of HCl, and is stopped when the introduction of HCl is stopped. When the Ga temperature was 850°C, the PH_3 flow rate was 5×10^{-5} mol/min, and the HCl flow rate was 5×10^{-5} mol/min, and the substrate temperature was 600°C, a 0.35- μ m thick GaP crystal was grown in five minutes. When the substrate temperature was changed while other conditions remained the same, the GaP crystal growth was possible within the substrate temperature range of 350°C to

800°C. Figs. 2(A) to 2(D) show reflection high energy electron diffraction (RHEED) images of the GaP crystal which was grown as described above. As the substrate temperature increases, the resultant crystal has good crystallinity. A GaP single crystal having the same (111) plane as that of the substrate can be obtained at the substrate temperature of 350°C or higher. Even if the Ga temperature is changed from 500°C to 900°C, the growth rate and the crystal quality are not affected.

Fig. 3 shows the relationship between a growth time and the thickness of a grown crystal film. The temperature of the Si substrate is 350°C. A GaP thickness on the Si (111) plane is increased in proportion to a growth time.

In this example, the opening portion 12D has the downwardly inclined portion and its opening end is substantially parallel to the substrate surface. However, the opening end of the downwardly inclined portion need not be parallel to the substrate. In addition, the opening portion 12D need not be inclined downward^{ly}, but can extend to be parallel to the substrate surface. Furthermore, the opening portion 12D can have a tapered nozzle portion whose opening faces the substrate surface.

Example 2

Figs. 4(A) and 4(B) show an epitaxial growth apparatus according to a second embodiment of the present invention. Differences between the first and second

embodiments are that the interior of the reaction tube 11 is partitioned by a partition wall 31 and that a substrate support table 32 is movable inside the reaction tube by means of a substrate moving rod 33. The seal method of the two ends of the reaction tube 11, the locations of the gas inlet and the gas outlet, and the electrical ovens for heating the reaction tube 11 are the same as those in the first embodiment, and are omitted from Figs. 4(A) and 4(B).

The Group III element 13 is stored in the boat 14 and is placed on the partition wall 31. An end portion 31A of the partition wall 31 on the downstream side of the gas flow is bent downward to guide the gas flow above the partition wall downward. The substrate support table 32 can be moved under the end portion 31A of the partition wall 31. The temperature inside the reaction tube 11 is controlled by the electrical ovens so that the high temperature is obtained at the position of the Group III element and the low temperature is obtained at the position of the substrate, in the same manner as shown in Fig. 1(C).

A GaAs crystal was grown on an Si (111) substrate using the apparatus shown in Figs. 4(A) and 4(B). The substrate 16 whose surface was cleaned in the same manner as described in Example 1 was located below the end portion 31A of the partition wall 31, as shown in Fig. 4(A). Ga was used as the Group III element. A gas mixture 34 containing arsine (AsH_3) and H_2 was flowed below the partition wall 31, and an H_2 gas 35 was flowed thereabove.

After air inside the reaction tube 11 had been sufficiently substituted, the reaction tube 11 was heated. After the temperature distribution inside the reaction tube as shown in Fig. 1(C) was obtained such that the Ga portion was at high temperature and the substrate position was at low temperature, for example, after the Ga portion (T_G) reached 850°C and the substrate temperature (T_G) reached 300°C to 700°C, HCl was mixed with the gas flow 35 to form a gas mixture containing ($HCl + H_2$). AsH_3 in the gas flow 34 was mainly decomposed in the form of As_4 by heat, and formed a gas mixture flow 36 containing ($As_4 + H_2$). Meanwhile, HCl was reacted with Ga to produce GaCl, and formed a gas mixture flow 37 containing ($GaCl + H_2$). The gas flow 37 containing the Group III element Ga and the gas flow 36 containing the Group V element As were flowed along independent flow paths, and were mixed for the first time near the end portion 31A of the partition wall 31. Then, these two gases reacted and a GaAs crystal 38 was grown on the substrate 16. Reference numeral 39 denotes an exhaust gas. GaAs precipitation and growth are started upon introduction of HCl, and stopped when the introduction is stopped. After the Ga temperature was 850°C, the substrate temperature was 600°C, the AsH_3 flow rate was 5×10^{-5} mol/min, and the HCl gas was flowed for five minutes at the flow rate of 5×10^{-5} mol/min, the reaction tube 11 was cooled and then the substrate 16 was unloaded. A 0.35- μ m thick GaAs crystal was grown on the substrate.

When the resultant crystal was observed by RHEED, the resultant crystal was a single crystal having the same (111) plane as that of the substrate when the temperature of the substrate 16 was 300°C or higher.

5 The GaAs crystal growth can be started and stopped not only by introduction of the HCl gas but also by moving the substrate. More specifically, the substrate support table 32 is located below the partition wall 31 so that the substrate 16 does not contact with the gas flow
10 37, the reaction tube 11 is heated to a desired temperature, and the HCl gas is mixed in the gas flow 35. In this state, the substrate support table 32 is moved to a position shown in Fig. 4(A), and the gas flows 36 and 37 can be mixed and reacted near the substrate surface. After
15 a predetermined period of time has passed, when the substrate support table 32 is moved below the partition wall 31 so as to separate the substrate from the gas mixing region, the GaAs growth is stopped. The quality of the resultant GaAs crystal and the growth rate in this case are
20 the same as those when the crystal growth is controlled by introduction of the HCl gas.

 The end portion 31A of the partition wall 31 on the downstream side of the gas flow is bent downward, so that the sectional area of the flow path of the gas flow 36
25 adjacent to the gas mixing region near the end portion 31A of the partition wall 31 is decreased. As a result, the velocity of the gas flow 36 is increased through the narrow

region, and an undesirable reverse flow of a gas and the like toward the flow path of the gas flow 36 can be prevented.

The moving mechanism of the substrate support
5 table can be added to the apparatus shown in Fig. 1(A).

Example 3

A GaP crystal was grown on an Si (100) substrate using the apparatus shown in Fig. 4(A). A substrate 16 was located at a position below the partition wall 31 so as not
10 to contact the gas flow 37. Only an H_2 gas was flowed as the gas flows 34 and 35. After ^{any} air inside the reaction tube 11 was sufficiently substituted, the reaction tube was heated by the electrical ovens to keep the temperature of the substrate 16 at $800^{\circ}C$ to $1,000^{\circ}C$ for 15 minutes, so
15 that contamination, a natural oxide film, and the like on the substrate were removed by cleaning. The temperature distribution inside the reaction tube was controlled as shown in Fig. 1(C), so that the Ga source portion was set at high temperature and the position of the substrate was
20 set at low temperature. In this example, the temperature T_S was kept at $800^{\circ}C$, and the temperature T_G was kept at $350^{\circ}C$ to $450^{\circ}C$. A gas mixture 34 containing PH_3 and H_2 and a gas mixture 35 of HCl and H_2 were introduced. After the gas flows were stabilized, the substrate was moved to the
25 downstream side of the end portion 31A of the partition wall 31, as shown in Fig. 4(A), and this state was maintained for five minutes. The gas flow 36 containing P_4

and the gas flow 37 containing GaCl were mixed and reacted near the end portion 31A, and as a result, GaP was grown on the substrate 16.

5 In this first step, a uniform amorphous GaP layer was grown on the Si substrate. The thickness of the GaP layer varies in accordance with the PH_3 and HCl flow rates and the substrate temperature. When the PH_3 flow rate was 0.1 ml/min and the HCl flow rate was 0.5 ml/min, the thickness was 20 nm.

10 Thereafter, the substrate 16 on which the GaP layer was grown was returned to a position at which it could not contact with the gas flow 37, e.g., a position below the partition wall 31, and HCl introduction was then stopped. In order to prevent P of the GaP layer deposited
15 on the substrate 16 from evaporating, the gas mixture flow 34 of H_2 diluted gas containing^a Group V element was flowed and then the substrate temperature was increased to 600°C to anneal the substrate. The gas mixture containing HCl and H_2 was again introduced. After the gas flow was
20 stabilized, the substrate 16 was moved to the downstream side of the end portion 31A of the partition wall 31, and the second-step growth was carried out. 10 minutes later, a 0.5- μm thick GaP monocrystalline layer was grown on the substrate 16. The resultant crystal had a full width at
25 half maximum of 40" of the X-ray rocking curve of the double crystal method. Thus, it was demonstrated that the resultant crystal had good crystallinity equivalent to that

of a crystal which was homo-epitaxially grown on a normal GaP substrate.

According to this embodiment, since the epitaxial layer is grown by moving the substrate 16 under the end portion 31A of the partition wall 31, a uniform
5 semiconductor film can be grown.

Fig. 5 shows a GaP growth rate characteristic on a substrate around a gas mixing region and a downstream region thereof. As can be seen from this characteristic,
10 the semiconductor growth rate around the gas mixing region near the end 31A of the partition wall 31 is noticeably high. Since this rate is much higher than a rate at which an oxide film is formed on the substrate surface, a hetero-epitaxially grown semiconductor of high quality
15 can be obtained at high yield.

Since the sectional area of the flow path of the gas flow 36 adjacent to the gas mixing region is smaller than the other portion of the flow path of the gas flow 36, a gas such as HCl which adversely affects the substrate
20 cannot flow to the upstream side of the gas flow 36 from the gas mixing region. For this reason, the substrate surface will not be contaminated with such gas before, during, and after semiconductor epitaxial growth onto the substrate.

25 As described above, the thickness of the GaP layer in the first-step growth varies in accordance with the growth conditions. When the PH_3 flow rate is

increased, the film thickness is increased as shown in Fig. 6. When the PH_3 and HCl flow rates were<respectively> fixed at 0.1 ml/min and 0.5 ml/min, the film thickness was increased as the substrate temperature increased, as shown in Fig. 7. The film thickness shown in Figs. 6 and 7 corresponds to that after a growth time of five minutes has passed.

Figs. 8(A), 8(B), and 8(C), respectively, show RHEED patterns of the GaP layers which were<respectively> obtained at the substrate temperatures of 500°C, 600°C, and 700°C. It is demonstrated that as the substrate temperature increases, crystallinity is improved, and a single crystal GaP having the same (100) plane as that of the substrate can be obtained at the substrate temperature of 600°C or higher. It can be considered that the grown film is annealed upon an increase in temperature during the transition from the first to second step, and the crystallinity is improved, thereby facilitating the growth in the second step.

Furthermore, after the amorphous GaP layer was grown on the substrate which was kept at 350°C, the substrate was not moved, and the HCl flow was stopped, thereby stopping GaP growth. Thereafter, the substrate temperature was increased up to 600°C. Thereafter, the HCl gas was again introduced to grow a GaP crystal on the substrate. The full width at half maximum of the X-ray rocking curve of the double crystal method was the same as

that of the GaP crystal obtained in the second-step growth by moving the substrate.

Example 4

GaP was epitaxially grown on an Si (100) substrate in combination of the method shown in Example 3 and the conventional method. After the first-step growth of GaP in Example 3, the substrate 16 was unloaded from the reaction tube. As described above, in this step, GaP on the Si (100) substrate is amorphous. GaP was then grown on this substrate by the conventional method.

The substrate on which the amorphous GaP layer was grown was placed at a position of the substrate 4 in the conventional apparatus shown in Fig. 11. Then, the temperature conditions shown in Fig. 11(B), i.e., the temperature at the position of the Ga source 3 of 900°C, the substrate temperature of 750°C to 800°C, and the temperature gradient at the position of the substrate of 5 to 10°C/cm were set while supplying the gas mixture 6 containing PH_3 and H_2 from the supply tube 5. Then, the gas mixture 7 containing HCl and H_2 was supplied to initiate epitaxial growth. After the epitaxial growth was performed for 20 minutes under the conditions of the PH_3 and HCl flow rates of 1 ml/min, respectively, a 2- μm thick GaP monocrystalline layer was grown on the substrate. The crystallinity of the resultant crystal was the same as that of the crystal shown in Example 3. The same result was

obtained when the second-step growth was conducted by the MOCVD method using trimethyl gallium and PH_3 .

In Examples 3 and 4, the first-step growth is started and stopped upon movement of the substrate.

5 Alternatively, the substrate can be initially located at the downstream side of the end portion 31A of the partition wall 31, and after the interior of the reaction tube 11 is set in the temperature distribution, i.e., the Ga source temperature is set at 800°C and the substrate temperature
10 is set at 350°C , amorphous GaP having a desired thickness can be grown on the substrate upon introduction of HCl. Thereafter, when the second-step growth was performed in accordance with the above examples, a single crystal having the same crystallinity could be obtained.

15 Group III-V compound semiconductor hetero-epitaxial growth on an Si substrate depends^{the fact} on that oxidation of an Si surface is suppressed to allow growth of a first Group III-V compound semiconductor thin film layer.

In the second-step growth of the present
20 invention, the first layer is grown on the Si (100) substrate at a relatively low temperature, as described above. When the first layer is grown at a high temperature of 500°C or higher, an oxygen component which is contained in the HCl gas and is produced by reaction of the reaction
25 tube and HCl is reacted with Si before growth of the GaP layer. Thus, the oxygen component forms an SiO_2 layer on the Si surface, and interferes with^{the} growth of the GaP

layer. When the substrate temperature is set at 450°C or lower, the GaP growth rate becomes faster than the SiO₂ growth rate, and a uniform film can be formed.

Fig. 9 is a graph showing the relationship between the substrate temperature and a covering ratio of the Si (100) substrate with the GaP layer. Fig. 9 reveals that a region on which no GaP is deposited is formed on the substrate at about 500°C. Therefore, in order to obtain a uniform GaP film, growth must be performed at 450°C or lower. The film which is grown at 450°C or lower does not always have good crystallinity and ^{is} found to have a quality between polycrystalline (450°) and amorphous (350°) upon observation by RHEED. Therefore, the film cannot be utilized for manufacturing a device such as an LED.

In the present invention, the second step is carried out at a temperature at which a film is to be grown normally by the VPE method, and after the amorphous or polycrystalline film of the first step is annealed, the GaP layer having good crystallinity can be grown thereon. This crystal can be utilized for manufacturing a device such as an LED.

Example 5

Fig. 10(A) is a sectional view of an epitaxial growth apparatus according to another embodiment of the present invention. The same reference numerals in Fig. 10(A) denote the same parts as in Fig. 1(A), and a detailed description thereof will be omitted. Although the

electrical ovens for heating the reaction tube 11 is omitted, they are controlled to heat the reaction tube to obtain the temperature distribution as shown in Fig. 1(C).

The principal difference between this embodiment and the embodiment shown in Fig. 1(A) is a gas introduction portion of a gas (containing a Group V element) (to be referred to as a Group V gas introduction portion hereinafter). A Group V gas introduction portion 41 has a gas inlet 41A at one end thereof. A supplied gas 21 is returned by the other end of the Group V gas introduction portion and continues to flow. The returning portion corresponds to a storage portion 41B of the substrate support table 42. An end portion 41C of the storage portion 41B is bent downward^s so as to guide a gas flow 24 containing a Group III element downward^{ly}. The two gas flows 23 and 24 are mixed and reacted at first time near the end portion 41C. The substrate support table 42 can be moved by the moving rod 42A inwardly and outwardly with respect to the storage portion 41B. A height from the substrate 16 supported on the substrate support table 42 to the end portion 41C must fall within the range within which mixing of the gas flows 23 and 24 is not interfered, and is preferably 1 mm to several cm, and more preferably 2 to 5 mm. The gas inlet 11E of the reaction tube 11 can have the same arrangement as that of Fig. 1(A).

This embodiment has^a good operability^{ta} such as easy^{and processability} change of the type of a Group III element or a substrate^{an}

used, easy cleaning of the interior of the reaction tube, and the like. The epitaxial growth of the Group III-V semiconductor using the apparatus of this embodiment can be performed in the same manner as in Examples 2 to 4.

5 Fig. 10(B) is a sectional view for explaining another embodiment for supplying gas flows in opposing directions. The same reference numerals in Fig. 10(B) denote the same parts as in Figs. 4 and 10(A). The operation of this embodiment is substantially the same as
10 that in the embodiment shown in Fig. 10(A), except that a gas flow 35 flowing through the source chamber is returned by the partition wall in the opposite direction and is then mixed with a gas flow 36 in the vicinity of an end portion 31A.

15 HBr or HI can be used instead of HCl as a gas which reacts with the Group III element and produces a halogenide gas.

 The hetero-epitaxial growth wherein a different material such as a Group III-V compound is grown on an Si
20 substrate has been described. The present invention can be applied to homo-epitaxial growth wherein a crystal is grown on a substrate of the same type of material, as a matter of course. The two-step crystal growth according to the present invention can be applied to other planes and other
25 substrates in addition to the Si (100) substrate, and can advantageously improve the quality of a grown crystal.

According to the present invention as described above, a substrate is placed in an H_2 gas atmosphere containing a Group V element, and a gas containing a Group III halogenide is mixed with the H_2 gas containing a Group V element immediately above the substrate, so as to grow a crystal. Therefore, a Group III-V compound semiconductor can be hetero-epitaxially grown on an Si substrate.

Therefore, electronic and optical devices using GaP, GaAs, and the like can be manufactured using an inexpensive Si substrate instead of an expensive Group III-V compound semiconductor substrate.

Since a Group III-V compound semiconductor crystal can be grown at a low substrate temperature of 600°C or lower, a highly functional device which is constituted by different materials and is arranged on an identical substrate can be realized.

20

25

What is claimed is:

1. An epitaxial growth method wherein a first gas
2 consisting of a hydrogen diluted gas containing a Group V
3 element is continuously flowed on a monocrystalline
4 substrate that is placed in a reaction chamber, said
5 monocrystalline substrate is arranged in a gas mixing
6 region where said first gas and a second gas containing a
7 halogenide of a Group III element are mixed adjacent to
8 said monocrystalline substrate, and a Group III-V compound
9 semiconductor is grown on said monocrystalline substrate.

2. A method according to claim 1, wherein the growth
2 of said Group III-V compound semiconductor is started and
3 stopped upon supply and termination thereof of said second
4 gas to said gas mixing region.

3. A method according to claim 1, wherein said
2 monocrystalline substrate is moved from a region that only
3 said first gas flows to the region of said first and second
4 gases mix, thereby growing said Group III-V compound
5 semiconductor on said monocrystalline substrate.

4. A method according to claim 1, wherein said
2 monocrystalline substrate is moved from a region that only
3 said first gas flows to the region of said first and second
4 gases mix, thereby growing said Group III-V compound

5 semiconductor on said monocrystalline substrate, and is
6 then returned to the region that only said first gas flows.

5. A method according to claim 4, wherein said
2 monocrystalline substrate is returned to said region that
3 only said first gas flows so as to stop the growth of the
4 semiconductor thereon.

6. A method according to claim 1, wherein said
2 monocrystalline substrate is a silicon substrate.

7. A method according to claim 1, wherein an end
2 portion of a flow path of said first gas adjacent to said
3 gas mixing region has a smaller sectional area than that of
4 the other portion of said flow path.

8. A method according to claim 1, wherein the
2 surface of said monocrystalline substrate is cleaned before
3 said monocrystalline substrate is placed in said reaction
4 chamber so as to remove a natural oxide film formed
5 thereon.

9. An epitaxial growth method comprising:
2 the first step of flowing a first gas consisting
3 of a hydrogen diluted gas containing a Group V element on a
4 monocrystalline substrate that is placed in a reaction
5 chamber, flowing a second gas containing a halogenide of a

6 Group III element along a flow path different from that of
7 said first gas, placing said monocrystalline substrate in a
8 gas mixing region where said first and second gases are
9 mixed, and growing a Group III-V compound semiconductor on
10 said monocrystalline substrate; and

11 the second step of further growing a Group III-V
12 compound semiconductor on said Group III-V compound
13 semiconductor grown by the first step.

10. A method according to claim 9, wherein the second
2 step comprises the step of flowing the first gas consisting
3 of the hydrogen diluted gas containing the Group V element
4 on said monocrystalline substrate that is placed in said
5 reaction chamber, flowing said second gas containing the
6 halogenide of the Group III element along a flow path
7 different from that of said first gas, placing said
8 monocrystalline substrate on said gas mixing region where
9 said first and second gases are mixed, and growing said
10 Group III-V compound semiconductor on said monocrystalline
11 substrate.

11. A method according to claim 9, wherein in the
2 first and second steps, the growth of said Group III-V
3 compound semiconductor is started and stopped upon supply
4 and termination thereof of said second gas to said gas
5 mixing region.

12. A method according to claim 9, wherein in the
2 first and second steps, said monocrystalline substrate is
3 moved from a region that only said first gas flows to the
4 gas mixing region that said first and second gases mix,
5 thereby growing said Group III-V compound semiconductor on
6 said monocrystalline substrate.

13. A method according to claim 9, wherein in the
2 first and second steps, said monocrystalline substrate is
3 moved from a region that only said first gas flows to the
4 gas mixing region that said first and second gases mix,
5 thereby growing said Group III-V compound semiconductor on
6 said monocrystalline substrate, and is then returned to the
7 region that only said first gas flows.

14. A method according to claim 13, wherein said
2 monocrystalline substrate is returned to said region that
3 only said first gas flows so as to stop the growth of the
4 semiconductor thereon.

15. A method according to claim 9, wherein in the
2 first or second step, the growth of said Group III-V
3 compound semiconductor is started and stopped upon supply
4 and termination thereof of said second gas to said gas
5 mixing region.

16. A method according to claim 15, wherein in the
2 remaining first or second step, said monocrystalline
3 substrate is moved from the region that only said first gas
4 flows to said gas mixing region that said first and second
5 gases mix, so that said Group III-V compound semiconductor
6 is grown on said monocrystalline substrate, and said
7 monocrystalline substrate is then returned to the region
8 that only said first gas flows to stop the growth of the
9 semiconductor.

17. A method according to claim 9, wherein in the
2 second step, said first and second gases are satisfactorily
3 mixed before gases reach the substrate in said reaction
4 chamber, and the gas mixture is supplied onto said
5 monocrystalline substrate that is held at a temperature
6 higher than a temperature in the first step, thereby
7 growing said Group III-V compound semiconductor.

18. A method according to claim 9, wherein said
2 monocrystalline substrate is a silicon substrate.

19. A method according to claim 9, wherein an end
2 portion of a flow path of said first gas adjacent to said
3 gas mixing region has a smaller sectional area than that of
4 the other portion of said flow path.

20. A method according to claim 9, wherein the
2 surface of said monocrystalline substrate is cleaned before
3 the first step so as to remove a natural oxide film formed
4 thereon.

21. An epitaxial growth apparatus comprising:
2 a first flow path, formed in a reaction chamber,
3 for flowing a first gas consisting of a hydrogen diluted
4 gas containing a Group V element;
5 a second flow path, formed in said reaction
6 chamber, for flowing a second gas containing a halogenide
7 of a Group III element; and
8 a support member for a monocrystalline substrate
9 arranged in said reaction chamber,
10 end portions of said first and second flow paths
11 in said reaction chamber being arranged so as to constitute
12 a mixing region where said first and second gases are
13 mixed, and
14 said support member displacing said
15 monocrystalline substrate in said mixing region, so as to
16 allow growth of a Group III-V compound semiconductor on the
17 surface of said monocrystalline substrate.

22. An apparatus according to claim 21, wherein said
2 support member for said monocrystalline substrate is
3 movable between said gas mixing region and a region that
4 only said first gas flows.

23. An apparatus according to claim 21, wherein the
2 end portion of said first flow path adjacent to said mixing
3 region has a smaller sectional area than that of the other
4 portion of said flow path.

24. An apparatus according to claim 23, wherein said
2 support member for said monocrystalline substrate is
3 movable between said gas mixing region and the region in which
4 only said first gas flows.

25. An apparatus according to claim 21, wherein said
2 first flow path is arranged parallel to said second flow
3 path.

26. An apparatus according to claim 21, wherein a gas
2 inlet of said first flow path is formed in said reaction
3 chamber so as to face a gas inlet of said second flow path.

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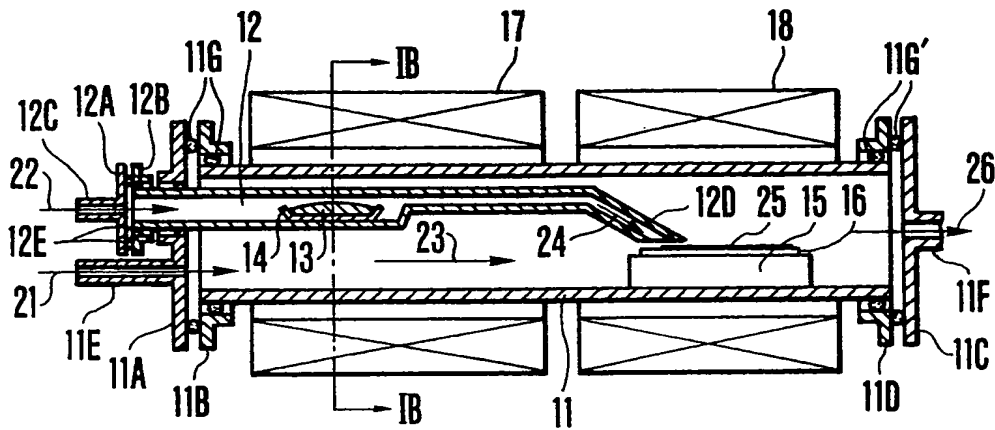


FIG. 1 (A)

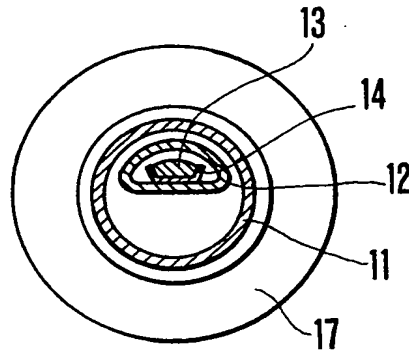


FIG. 1 (B)

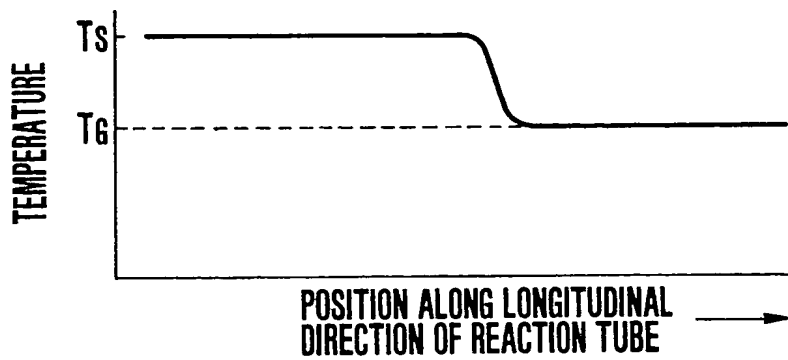
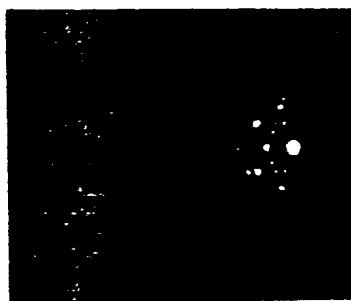


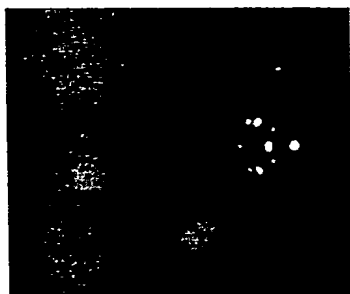
FIG. 1 (C)

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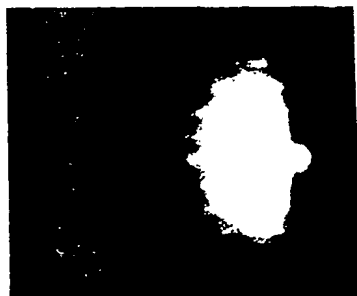
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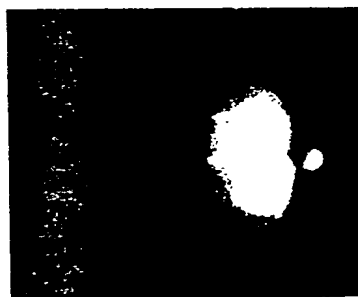
SUBSTRATE
TEMPERATURE 450°C



SUBSTRATE
TEMPERATURE 400°C



SUBSTRATE
TEMPERATURE 350°C



SUBSTRATE
TEMPERATURE 300°C

FIG.2(A) FIG.2(B) FIG.2(C) FIG.2(D)

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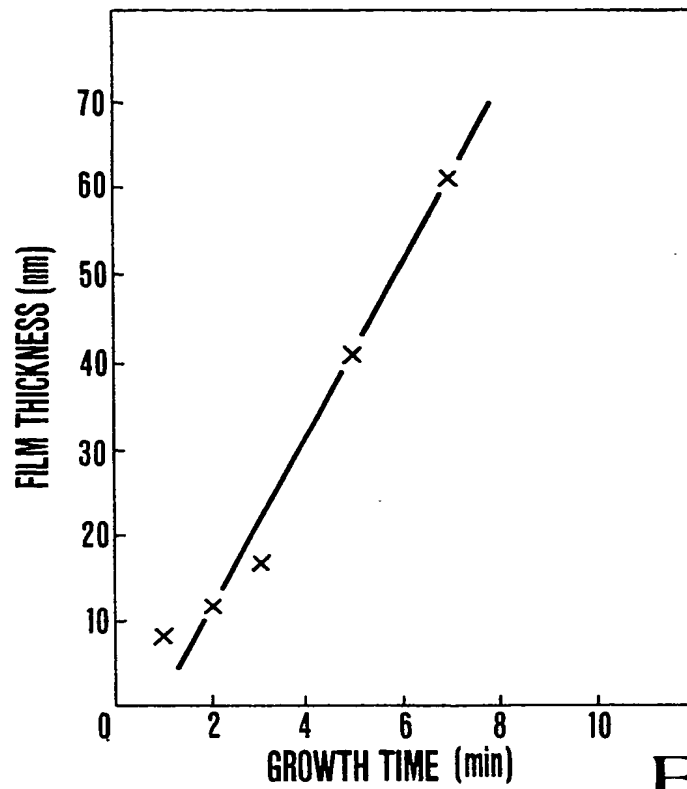


FIG. 3

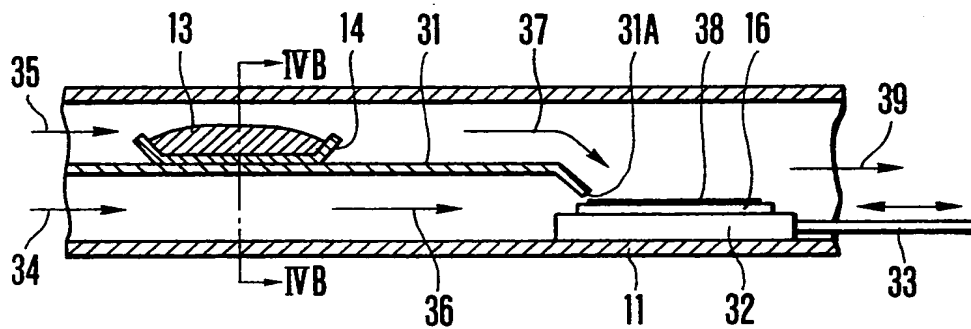


FIG. 4 (A)

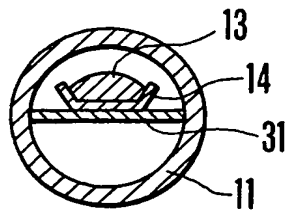


FIG. 4 (B)

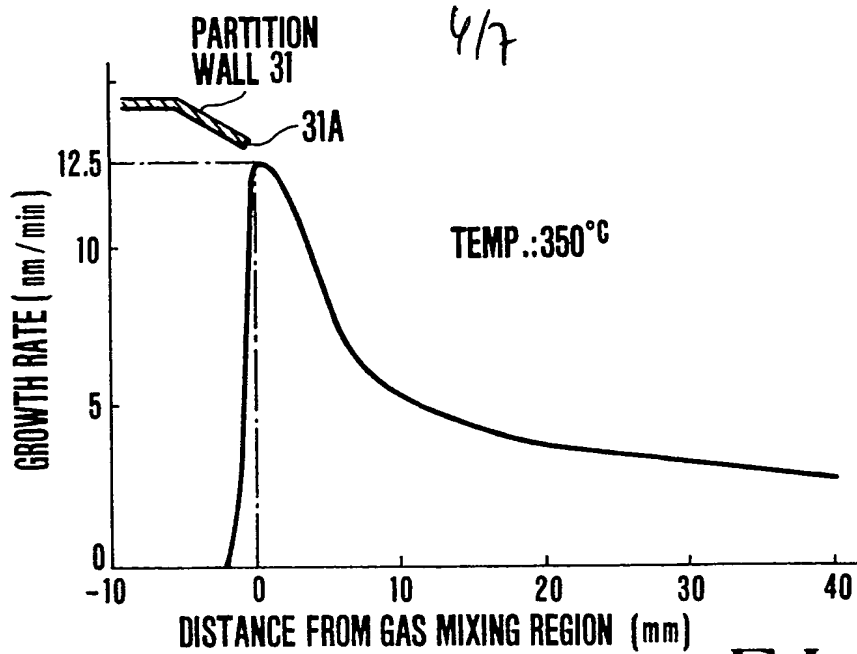


FIG.5

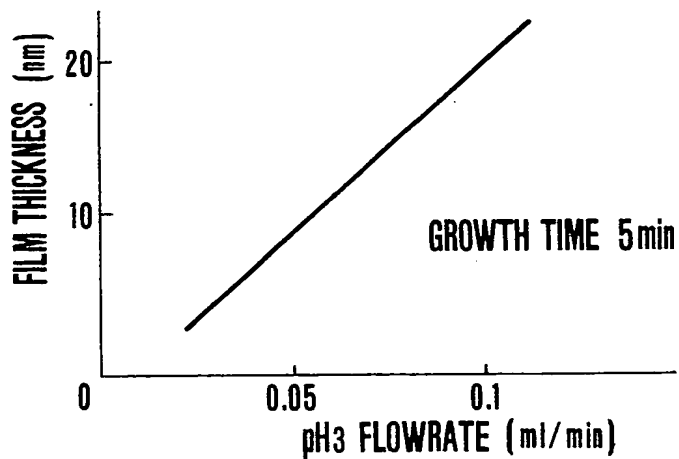


FIG.6

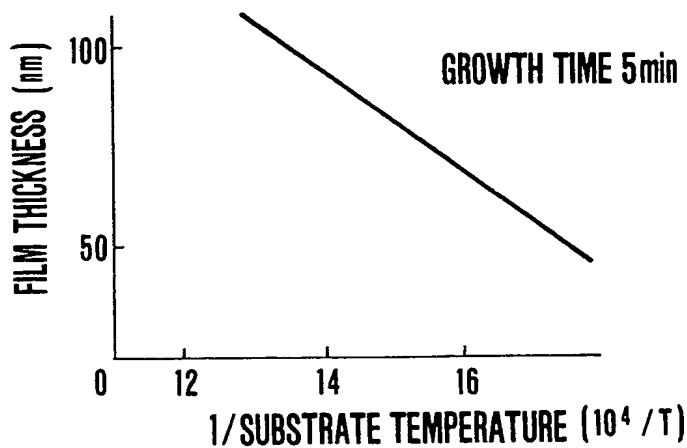


FIG.7

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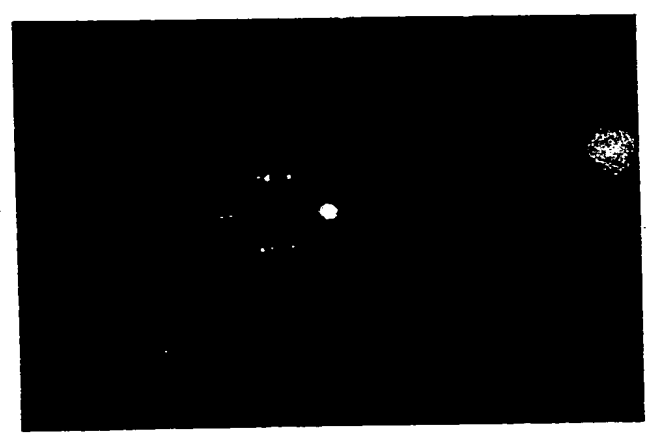
SUBSTRATE TEMPERATURE 700°C
CRYSTALLINITY SINGLE CRYSTAL
(KIKUCHI PATTERN)

FIG.8 (C)



SUBSTRATE TEMPERATURE 600°C
CRYSTALLINITY SINGLE CRYSTAL

FIG.8 (B)



SUBSTRATE TEMPERATURE 500°C
CRYSTALLINITY FIBER STRUCTURE

FIG.8 (A)

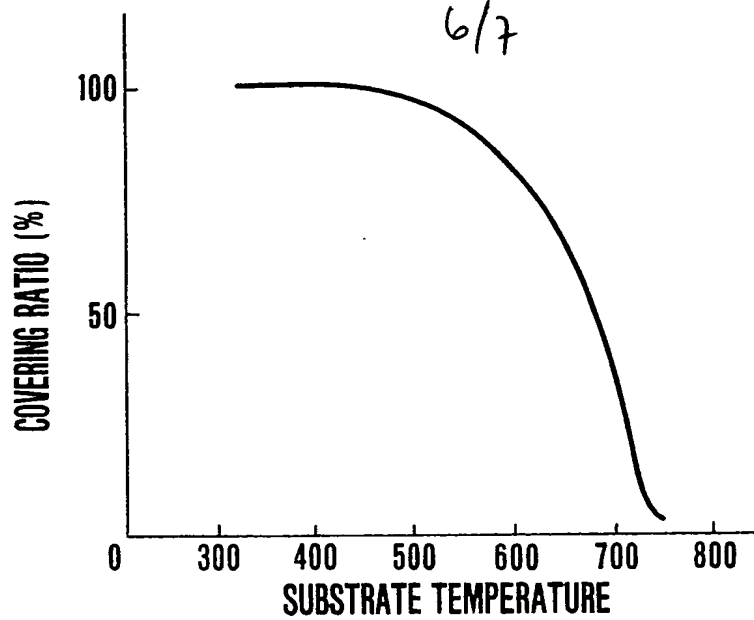


FIG. 9

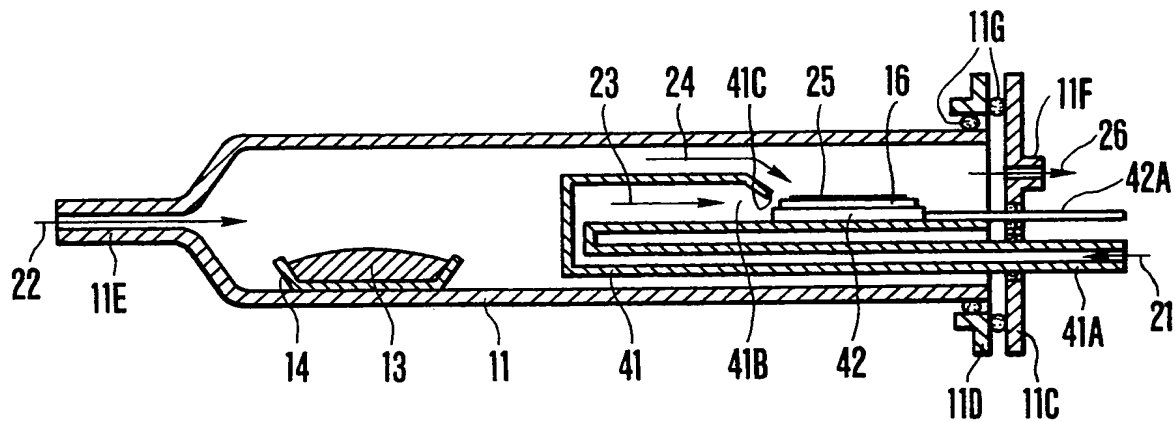


FIG. 10(A)

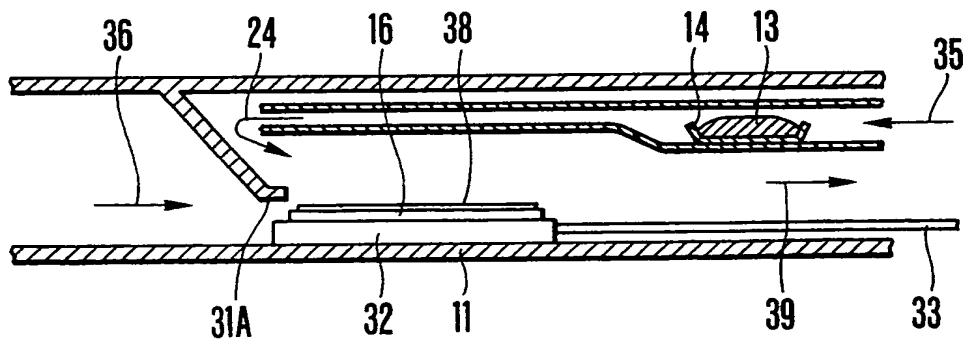


FIG. 10(B)

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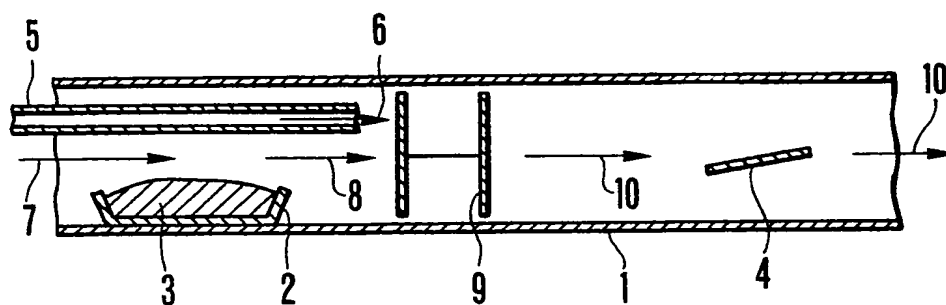


FIG. 11 (A)
(PRIOR ART)

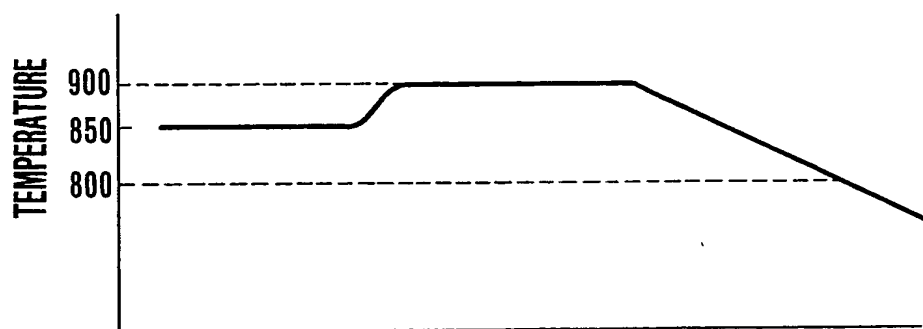


FIG. 11 (B)
(PRIOR ART)



European Patent
Office

EUROPEAN SEARCH REPORT

0238830
Application number

EP 87 10 2014

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A-2 055 774 (PLESSEY) * Figure 1; page 2, lines 21-41 *	1,2	C 30 B 25/14 C 30 B 25/18 C 30 B 29/40
A	US-A-4 504 329 (QUINLAN et al.) * Figure; column 4, lines 19-23,59-68; column 5, lines 1-17 *	1,6,21	
A	US-A-4 561 916 (AKIYAMA et al.) * Claim 1 *	1,6,9 10,17 18	
A	US-A-4 180 825 (MASON et al.) * Abstract; column 3, paragraph 1 *	1,6,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 30 B 25/00 C 30 B 29/00 H 01 L 21/00 C 23 C 16/44
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-07-1987	Examiner PATTERSON A.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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